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Electrophilic Phosphinidenes: Science or Fiction?

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Helen Jansen

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aan mijn ouders

Preface

Electrophilic phosphinidenes are versatile, transient intermediates that have been highly valuable in the synthesis of a plethora of organophosphorus compounds. However, as the title of this thesis suggests, their existence has never been proven unequivocally. It has even been pointed out by Prof. F. Mathey that "… in almost every case, it is possible to conceive alternative mechanisms, which do not involve phosphinidenes". Therefore, we decided to investigate both the formation and reactivity of phosphinidenes in detail. In doing so, we particularly focused on the newly, in-house developed phosphinidene precursors, the so-called phosphepines.

In our research on the reactivity of electrophilic phosphinidenes, we present in the first chapter (*Chapter 1*) a literature study explaining the general concept of the valence isomerization of the phosphepines and their analogues that ultimately leads to the electron-deficient transients. This study starts by reviewing the valence isomerization of the all-carbon cyclohepta-1,3,5-triene into the corresponding bicyclo[4.1.0]hepta-2,4-diene and is followed by the seven-membered ring systems bearing the elements O, S, N and P, while focusing on the parent systems and their synthetic applications.

Secondly, we describe a case study in *Chapter 2* that illustrates the reactivity of the transient phosphinidenes [R–P=W(CO)$_5$] (R = Me, Ph), which are generated thermally from the corresponding benzophosphepines. We will compare the reaction outcome with the results obtained from the electrophilic phosphinidenes generated via the classical 7-phosphanorbornadienes developed by Prof. F. Mathey, to illustrate the advantages of our method.

Whereas electrophilic phosphinidene complexes might have been termed fictitious by the skeptical scientist, the content of *Chapter 3* convincingly demonstrates by employing electrospray ionization tandem mass spectrometry

(ESI-MS/MS), solution-phase chemistry and density functional calculations that the transient phosphinidenes [R–P=$W(CO)_5$] are true entities of scientific value.

Chapter 4 presents a detailed computational investigation on the valence isomerization of the seven-membered phosphepines to the phospha-norcaradienes at the B3PW91/6-311+G(d,p) level of theory. The influence of benzannulation, complexation, oxidation and the substituent at phosphorus was studied with the ultimate aim to investigate if the amino-substituted derivatives can be used as suitable phosphinidene precursors for the in-situ generation of singlet aminophosphinidenes [R_2N-P].

Chapter 5 describes the remarkable chemistry of ^{Me}BABAR-Phos, which is a sterically unshielded phosphirane that can be obtained via phosphinidenoid chemistry. Combining ^{Me}BABAR-Phos and methyl triflate affords an amino-stabilized phosphiranylium ion, which undergoes various nucleophilic addition reactions, resulting in P-substituted phosphiranes and a NHC-stabilized phosphiranylium cation.

Hilversum, 23 augustus 2010

Helen Jansen